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(12) UK Patent Application (19) GB (11) 2 058 379 A

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(21) Application No 7931589  
(22) Date of filing 12 Sep 1979  
(43) Application published  
8 Apr 1981

(51) INT CL<sup>3</sup>  
G03C 1/00 B41M 5/00  
G03C 1/68

(52) Domestic classification  
G2C 1B1X 1B3B C6A  
B6C 301 307 30X 313  
601 602 605 606 630 631  
640 HD SAD

(56) Documents cited  
None

(58) Field of search  
G2C  
G2X

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(54) Imaging Process

(57) Process for recording information  
by image-wise deposition of hydrosol  
particles through chemiphoresis  
wherein said particles are coagulated  
imagewise onto an image-wise

pattern defined by metallic cations  
which act as a coagulant for a  
hydrosol, the resulting pattern of  
deposited hydrosol particles e.g.  
deposited on an aluminium support  
being suited for use as planographic  
printing plate.

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# SPECIFICATION

## Process for Recording Information by Image-wise Deposition of Hydrosol Particles Through Chemiphoresis

- The present invention relates to a process for recording information by image-wise deposition of hydrosol particles through chemiphoresis.
- According to Dennis C. Prieve et al, in their article: "Chemiphoresis, a method for deposition of polymer coatings without applied electric current"—Ind. Eng. Chem. Prod. Res. Dev., Vol. 17, no. 1, (1978) p. 32, chemiphoresis is defined as a mechanism in which an electroless process occurs at a solid electrolyte interface to produce ions causing local coagulation and deposition of a hydrosol.
- Chemiphoretic deposition of a hydrosol differs from electrophoretic deposition in that the coagulant is generated by chemical means rather than by applied voltage.
- Chemically initiated generation of ions is utilized to coagulate latex particles to form a resin film upon the surface of metals e.g. a steel surface. The source of ions is the regulated dissolution of iron immersed in a formulation of acid plus latex. Iron atoms on the steel surface dissolve and produce hydrolyzable cations. The cations adsorb on the surface of suspended latex particles adjacent to the iron surface. The negative charge of the latex is neutralized, whereupon a membrane layer deposits on the iron. Thereafter, the continuing dissolution of the iron provides cations, which diffuse through the accumulating porous film. The rate of deposition is controlled by the diffusion of cations through the membrane. So, at last a smooth continuous film is obtained by allowing the latex particles to coagulate at a temperature at which they are sufficiently soft.
- The present invention provides a process for recording information wherein an image-wise pattern is formed on a recording material and particles are coagulated onto said image-wise pattern to form a permanent record thereof, characterized in that the said image-wise pattern is defined by metallic cations which act as a coagulant for a hydrosol, and a hydrosol which is coagulated by said ions is contacted with the said ions under conditions whereby the hydrosol becomes coagulated to define the said image-wise pattern.
- By hydrosol is understood a composition of matter wherein colloid particles move by Brownian motion in an aqueous carrier liquid. The colloid particles are of inorganic nature, e.g. oxides, hydroxides or sulphides of metalloids or metals e.g.  $\text{SiO}_2$  or  $\text{Ag}_2\text{S}$  or of organic nature, e.g. polymer particles. In the latter case the hydrosol is also called a latex. Since patterns of polymer films find a broad application e.g. as resist or printing form the present invention provides a process to form such patterns e.g. photographically.
- Metallic cations which are particularly suited for acting as a coagulant for a hydrosol are metal ions having at least two unitary positive charges per ion in other words multivalent metal cations. Examples of such cations are  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{V}^{5+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$ ,  $\text{Ni}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ge}^{4+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Nb}^{5+}$ ,  $\text{Mo}^{6+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Sb}^{5+}$ ,  $\text{Ta}^{5+}$ ,  $\text{W}^{6+}$ ,  $\text{Pb}^{4+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Bi}^{5+}$ ,  $\text{Ce}^{4+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Pa}^{4+}$  and  $\text{U}^{4+}$ .
- The image-wise pattern may be formed for example by image-wise applying a liquid containing the said ions in dissolved form to the recording material. In another procedure the image-wise pattern is provided by image-wise applying to the recording material a metal, metal oxide, metal base or metal salt which is capable of providing said ions when in contact with the aqueous phase of the applied hydrosol. For that purpose the recording material may be e.g. paper, resin film material, glass, ceramic, stone or wood. When the ions are applied from a liquid the image-wise coating is effected advantageously on a liquid-absorbing material. For example a porous material e.g. porous paper or a hydrophilic colloid layer, e.g. gelatin layer. The liquid containing said ions may be applied by any method, e.g., with a pen, typewriter keys, ink-jet device or applied e.g. as an aerosol through the openings of a stencil pattern or mask. When a metal, metal oxide, metal base or metal salt capable of providing said ions is used such material may be applied image-wise, e.g. by painting from a dispersion or by vapour deposition, e.g. through a mask.
- According to a particular embodiment said ions are derived from a source of ion-providing substance which is overall available in at least one layer or support member of said recording material and said recording material by image-wise applied activating energy is modified structurally such that an initially blocked ion-source is unblocked i.e. made capable to deliver image-wise said ions by contact with a solvent for said ions, or modified structurally such that said source of ions is blocked image-wise so that a solvent for said ions can not reach the ion providing substance in area of the recording material which have been modified structurally by the image-wise applied energy.
- The activating energy is e.g. electromagnetic radiation energy including all types of radiation known in photography and radiography, energy associated with high velocity elementary particles e.g. energy delivered by fast electrons, heat energy or mechanical energy in the form of pressure.
- In an example of the embodiment wherein the ion-source is initially blocked said recording material contains a layer that initially is overall impermeable to said ions, and which becomes permeable to said ions on exposure to said activating energy.
- In another particular embodiment said ion-source is covered by a layer which initially is overall impermeable to said ions, and said layer becomes impermeable to said ions on exposure to said activating energy.

According to another particular embodiment said ions are image-wise delivered by a recording material that contains a layer that initially is impermeable to said ions and wherein parts of said layer are image-wise removed after image-wise exposure to said activating energy, allowing thereby the image-wise extraction from said material of said ions with a liquid contacting said recording material.

In a particular example of the embodiment proceeding with an image-wise unblocking of an ion-source a photographic material is used which comprises a support having thereon a binder containing numerous vesicles, each vesicle comprising membranes containing lipids and rhodopsin and inside said vesicles

(a) metal cations or

(b) chelatometric materials.

On image-wise exposure to light, the metal cations can flow through the photoexposed vesicle walls and can cause image-wise chemiphoretic hydrosol-coagulation according to the invention. The preparation of vesicles having membranes of rhodopsin and lipids and containing inside e.g. cobalt (II), manganese (II), europium (III), copper (II) and calcium ions is described in the United States Patent 4,084,967.

Other recording materials suitable for use according to the present invention are e.g. photographic, thermographic or pressure-sensitive materials in which through the image-wise action of photons, heat or pressure an image-wise change in permeability of a recording layer incorporating or covering the substance or substances yielding said ions can be obtained.

Another recording material suitable for use according to the present invention contains a recording layer that as a result of the image-wise action of electromagnetic radiation, and/or heat obtains an image-wise change in solubility and/or mechanical and/or chemical removability, whereby said layer can be image-wise removed, e.g. by wash-off from an underlying overall applied ion source from which the chemiphoretically active ions can be released by means of an aqueous liquid.

A further recording material for use in the present invention is a pressure-sensitive material containing the ion-yielding substance or substances in microcapsules the membranes of which are rupturable by pressure so that the ions can be set free image-wise by image-wise applied pressure.

Still another recording material suitable for use according to the present invention is a recording material that contains non-differentially ion-precursor substances e.g. a photosensitive substance that yields hydrogen ions on photoexposure by reaction with water as described e.g. in the United States Patent 3,522,049. Hydrogen ions that are formed photographically may be used to image-wise attack a metal substrate and produce thereby image-wise metal ions e.g. iron or zinc ions that in accordance with the present invention are allowed to act as a coagulant for a hydrosol.

In a further embodiment of the present invention the recording material containing initially an ion-source that is capable of providing non-differentially said ions is image-wise covered with a substance blocking in the recording material the release of said ions with a solvent therefor.

A recording material suitable for use in that embodiment is any material capable of providing non-differentially said ions but wherein or whereon the ion release can be blocked by an image-wise deposit of a substance or substances stopping ion release by chemical reaction or by shielding the ion releasing substance from the action of a solvent for said ions. For example such recording material is an image receiving material used in a photographic silver complex diffusion transfer reversal process (DTR-process) wherein a silver image is deposited onto a receiving material containing ions or an ion releasing substance capable of releasing such ions in contact with an aqueous liquid.

Other recording materials useful in the present invention comprises a photoresist layer e.g. on top of a metallic layer e.g. aluminium layer acting as said ion-source.

In the photoresist field two types of compositions are considered. The negative-acting photoresist compositions that are rendered insoluble in the exposed areas and the positive acting photoresist compositions that become more soluble in the exposed parts.

In a specific embodiment of the process according to the present invention a negative acting photoresist layer is applied onto a material e.g. a metallic layer or sheet which is capable of providing said cations and after image-wise photoexposure is removed in the non-exposed parts uncovering thereby the portions of the ion-providing material corresponding with said non-exposed parts.

In another specific embodiment of the process according to the present invention a positive acting photoresist layer is applied onto a material e.g. layer or sheet which is capable of providing said cations and after image-wise photoexposure is removed in the exposed parts uncovering thereby the portions of the ion-providing material corresponding with said exposed parts.

A survey of negative acting and positive acting photoresist materials is given by W. S. De Forest in his book "Photoresist Materials and Processes" McGraw-Hill Book Company (1975). Among these photoresist compositions are especially mentioned the Shipley (a Trade Mark) resist compositions of Shipley Company Newton, Mass. U.S.A. They usually contain novolaks that are sensitized, e.g. with quinone diazide compounds. Sensitized positive working novolak resists are described in the U.S. Patent Specifications 3,201,239 and 3,666,473. Photoresist compositions of the negative working type that contain novolak and a light-sensitive nitrone are described, e.g., in the U.K. Patent Specification 1,069,383. Negative working photoresists on the basis of polyvinyl cinnamate are described, e.g., in the U.S. Patent Specification 2,732,301.

Particularly suited photosensitive photoresist layers are photopolymerizable layers comprising a hydrophilic, macromolecular organic polymer dispersion medium including a dispersed phase containing:

1. at least one ethylenically unsaturated monomer having a boiling point above 100°C at normal atmospheric pressure and being capable of forming a high polymer by free-radical initiated, chain-propagating addition polymerization, and
  2. in reactive association with said monomer at least one free-radical photo-initiating compound, e.g. an oxime ester as described in the U.S. Patent Specification 3,558,309. Suitable monomers for that photopolymerization system are described e.g. in the U.S. Patent Specification 3,718,473. After photopolymerization the non-polymerized parts of the recording layer need not be removed by means of solvents. The photopolymerized layer shows image-wise differentiation in permeability, e.g. for etchants for an underlying layer or support e.g. metal layer or support yielding the chemiphoretically active ions suitable for use according to the present invention. Metal ions that are particularly suitable are the multivalent metal ions  $Al^{3+}$ ,  $Bi^{3+}$  and  $Fe^{3+}$ .
- According to a particular embodiment a composite photosensitive recording material suitable for use in the present invention contains on top of the photoresist layer, which covers the metallic layer that acts as a source of said metallic cations, a silver halide emulsion layer or a layer containing development nuclei suitable for silver image formation by the silver salt complex diffusion transfer process (DTR-process). Said composite material exhibits increased photosensitivity in that through the high photosensitivity of the silver halide first with a low intensity image-wise exposure a silver metal image can be formed serving as a mask for image-wise irradiation of the underlying less photosensitive photoresist layer. The silver halide emulsion layer may be of the negative or positive type, i.e. yielding a silver image in correspondence either with the exposed or unexposed areas. The use in photoresist image production of reversal processed silver halide emulsions, prefogged silver halide emulsions, silver halide emulsions that are capable of being processed by photosolubilization, and silver halide emulsions that on development produce mainly an internal latent image and on subsequent processing provide a direct-positive image is described, e.g., in U.K. Patent Specification 1,227,603. Herein also the combined use of a photoresist layer and a receptor layer comprising development nuclei for the DTR-process as silver-mask-forming layer is mentioned.
- According to a preferred embodiment silver metal is image-wise deposited by the DTR-process directly on a metal substrate, e.g. on an aluminium sheet as described e.g. in the U.S. Patent Specification 3,186,842, so that the silver image serves as an image-shield for blocking the extraction of said cations e.g.  $Al^{3+}$  ions from said substrate. Said embodiment is preferred for its convenience and while it operates with known highly photosensitive silver halide emulsion layer DTR-materials which can be exposed in the classical graphic art dark room cameras.
- In a particular procedure of that embodiment the DTR-process proceeds with a direct-positive type silver halide emulsion layer so that after exposure to an original and silver complex transfer and development hydrosol deposition in accordance with the opaque areas of the original is obtained. When, however, an internegative is applied in the photo-exposure, a common negative type emulsion layer is used for obtaining through the DTR-process a silver image in an image receiving material wherein the silver image blocks ion release in correspondence with the more opaque areas of the internegative and consequently in correspondence with the more transparent areas of the original from which the internegative has been produced.
- The process for producing a DTR-silver image on an image receiving material for image-wise blocking the release of said cations from said material comprises the steps of:
- 1) exposing to an original a light-sensitive silver halide emulsion layer of a photographic material,
  - 2) contacting the image-receiving material with the image-wise photoexposed silver halide emulsion layer while wetted with an aqueous alkaline liquid in the presence of at least one developing agent capable of reducing photoexposed silver halide to cause development of the developable silver halide and to cause undeveloped silver halide to become complexed with a silver halide complexing agent and to transfer to the image-receiving material on or in which the complexed silver halide becomes converted to a silver or silver-containing image, and
  - 3) separating said photographic and image-receiving materials.
- For particulars about exposure and developing apparatus, which may be applied in the DTR-process for use according to the present invention reference is made e.g. to "Photographic Silver Halide Diffusion Processes" by A. Rott and E. Weyde, Focal Press, London-New York (1972).
- The image-receiving layer or sheet in or on which a silver image can be formed according to the diffusion transfer process using a silver halide emulsion, normally forms part of a separate element. However, it is likewise possible to use a so-called "mono-sheet" material wherein the light-sensitive layer and an image-receiving layer or sheet are present in one and the same material, such layers being carried by the same support and to remove the silver halide emulsion layer e.g. by stripping or wash-off after the silver image on the receiving element has been formed. Such procedure is described e.g. in the U.K. Patent Specification 1,253,518.
- The image-receiving layer or sheet or a layer adjacent thereto may contain one or more agents for promoting the reduction to metallic silver of the complexed silver salt, these agents being called

development nuclei. Such development nuclei have been described in the above-cited publication by A. Rott and E. Weyde, p. 54—57. Preferably nickel sulphide nuclei are used. Development nuclei can also be incorporated into the processing liquid as is described in the United Kingdom Patent 1,001,558, filed April 13, 1962 by Gevaert Photo-Producten N.V.

When using an aluminium substrate as silver image-receiving material no developing nuclei are needed since the aluminium itself acts in the electrochemical reduction of the silver complexes to silver.

In order to improve the blocking power for ion release of the deposited silver image the silver image is rendered hydrophobic by a chemical after-treatment with an organic compound reacting with silver ions.

The silver can be rendered hydrophobic by different methods e.g. by an oxidizing treatment followed by a treatment with organic compounds reacting with silver ions. For example oxidation with hexacyanoferrate (III) ions in the presence of metal salts such as halides forms insoluble silver salts. According to another method the silver image after oxidation is converted with a liquid containing organic compounds having —SH, —SeH, isothiocyanate, —OH or —NH— group(s) into sparingly soluble complex compounds as described e.g. in the already mentioned book of A. Rott and E. Weyde pages 105—116 said liquid being called lithographic preparation and sometimes also called a fixer.

After hydrophobic polymer particles are deposited image-wise by chemiphoresis on an aluminium sheet in the areas that are not shielded by the silver image the silver image portions even when hydrophobized can be removed to uncover the aluminium again. Such may proceed with common silver etch or bleaching liquids containing an oxidizing agent e.g. bichromate ions in acid medium. The bared aluminium portions are hydrophilic so that said procedure applies advantageously in the production of a planographic printing form.

The electroless hydrosol deposition proceeds advantageously with latex polymers i.e. polymer particles dispersed in aqueous medium and which for that purpose may be prepared by emulsion polymerization. The aqueous dispersion of a homopolymer or copolymer is prepared e.g. by radical polymerization in emulsion of one or more polymerizable monomers according to known techniques, e.g., those described by Sorenson and T. W. Campbell, Preparative Methods of Polymer Chemistry, Interscience Publishers, New York (1961). In this radical polymerization use is made of dispersing agents such as those described by K. Laux, "Die Grenzflächenaktiven Stoffe" in Winnacker-Kühler's "Chemische Technologie" Carl Hanser-Verlag; Munich (1960) pp. 155—242.

Aqueous dispersions of polymers prepared by dispersing a solution of a non-water-soluble polymer in a water-immiscible solvent in an aqueous solution are likewise applicable. As solvents may be mentioned, e.g., chlorinated hydrocarbons such as methylene chloride and trichloroethylene.

Further polymer dispersions that are appropriate for being applied in the present invention are obtained by mechanically dispersing in water finely divided polymer particles preferably with the help of surfactants and/or hydrophilic colloids such as polyvinyl alcohol and gelatin. However, latexes obtained by aqueous emulsion polymerization are usable directly and are therefore preferred. In this polymerization technique the monomer(s) is (are) dispersed by stirring so as to form very fine droplets in the presence of water, emulsifiers (e.g. soaps, ammonium oleate, sulphonated fatty alcohols and the like) protective colloids (carboxymethylcellulose, polyvinyl alcohol and the like), optionally a buffering system, a surfactant and a water-soluble catalyst, e.g. hydrogen peroxide or a persulphate. The polymer or copolymer is obtained in the form of a stable dispersion of polymer particles in water.

The dispersed polymer particles may size from 0.01  $\mu\text{m}$  to 50  $\mu\text{m}$ . However, the larger the particles, the less the resolving power on image-wise deposition. An average particle size of 0.20 to 0.02  $\mu\text{m}$  is very suitable. The amount of dispersed polymer particles in the coating liquid is not critical and good results are obtained, e.g., when aqueous dispersions are used containing from 10 to 0.1% by weight of dispersed polymer.

The polymer droplets may contain all kinds of ingredients suitable in the image detection and helping in yielding or emphasizing some physical or chemical characteristics of the deposited latex pattern. For example, the latex particles may contain substances increasing the hydrophobicity of the chemiphoretically deposited particles that are applied e.g. in the production of a planographic printing form. In that respect are mentioned organic fluorine and silicone compounds, further all kinds of pigments and dissolved dyes that provide, e.g., colour and/or greater mechanical strength to the polymer deposit. For colouring purposes azo dyes and carbon black may be used. Other pigments have, e.g., photoconductive properties, such as zinc oxide or are used as whitening agent, toothng agent or filler, such as titanium dioxide, silica, alumina, kaolin, barium sulphate or a combination of at least two of these substances.

Other ingredients are chemically active or can be activated and may act, e.g., as curing agent, e.g. cross-linking agent, thermosetting catalyst or polymerization initiator, e.g. photoactive polymerization initiator. For example when the dispersed particles contain cross-linkable polymers or still polymerizable monomers curing may be effected by catalysts or radical-forming compounds in order to modify or change the properties of the image-wise chemiphoretically deposited material e.g. with regard to wettability, mechanical strength of the deposit or adherence to its support.

Suitable radical-forming photoinitiators, and polyethylenically unsaturated cross-linking agents

are described, e.g., in the United States Patents 3,558,309 and 3,178,473.

In the embodiments where the latex deposition has to result in a finally impermeable resin deposit without a special after-heating, latex particles are used whose glass-transition temperature ( $T_g$ ) is below 25°C.

- 5 Polymers with a  $T_g$  below 25°C are described, e.g., by D. H. Solomon in "The Chemistry of Organic Film Formers" John Wiley & Sons, Inc. New York (1966) p. 27. Examples thereof are: 5

	poly(methyl acrylate)	$T_g: 8^\circ\text{C}$	
	poly(ethyl acrylate)	$T_g: -22^\circ\text{C}$	
	poly(n-propyl acrylate)	$T_g: -55.5^\circ\text{C}$	
10	poly(n-butyl acrylate)	$T_g: -54^\circ\text{C}$	10
	poly(n-butyl methacrylate)	$T_g: 20^\circ\text{C}$	

By preparing copolymers from monomers that produce homopolymers with low  $T_g$ , e.g. below 10°C, and from monomers that produce homopolymers with high  $T_g$ , e.g. above 50°C, such as styrene yielding poly(styrene) with  $T_g$  100°C, a large variety of copolymers with a  $T_g$  below or above 25°C can be obtained.

- 15 An example thereof is an acrylonitrile-butadiene-styrene (ABS) terpolymer having a  $T_g$  of 10°C. 15

An alternative method of modifying the  $T_g$  is to add a low molecular weight compound as plasticizer for the polymer or copolymer.

- As far as the mechanism of chemiphoretic latex deposition is concerned, one possible role of the active ions, e.g. aluminium or iron ions, is to neutralize the charge on the latex particles. The rate of polymer deposition is controlled by the flux of ions leaving the recording material in a more or less strong solvent. This process is controlled by the diffusion of said ions through the porous polymer film that is gradually closed. Chemically said ions can be set free e.g. from a solid salt, base or metal. In that respect the use of an acid is very effective, e.g. in conjunction with an aluminium- or iron-containing plate, e.g. steel plate. For example an aqueous acid solution of pH 1 to 2 is very effective and can serve as dispersing medium for latex particles of the kind of the above terpolymer.

- Iron may be very effectively dissolved and iron ions obtained by the use of an aqueous solution of hydrogen fluoride either or not in conjunction with hydrogen peroxide. In the presence of hydrogen peroxide  $\text{FeOH}^{2+}$  ions are formed that adsorb on latex particles stabilized by a negative charge and effect neutralization of that charge resulting in latex coagulation.

- The process for recording and/or reproducing by image-wise deposition of hydrosol particles through chemiophoresis is suited, e.g., for the production of planographic printing plates wherein, e.g., a hydrophobic latex-deposit is used on a water-accepting i.e. hydrophilic plate, e.g. aluminium plate. The latex or latex mixture to be deposited has to form a firm and strongly adhering film to the substrate e.g. aluminium sheet when such is used as planographic printing form. Therefore the latex polymer without impairing too much its hydrophobic character contains a certain amount of structural repeating units having a polar character e.g. units including a nitrile group, a hydroxyl group or carboxyl group. An example of such polymer is a copoly(butadiene/methylmethacrylate/itaconic acid) (47.5/47.5/5 percentages by weight). Further the process can be applied in the production of stencil or screen printing masters, electrical conductivity patterns, latex polymer etch resist patterns and swellable patterns of latex polymer serving as hectographic master wherefrom dyestuff or dyestuff precursor can be extracted with a transfer liquid. In hectography the transfer of the dye or dyestuff precursor proceeds onto suitable receptor sheets, whereby a plurality of dye images is formed in repeated transfer steps.

- 45 The present invention is illustrated by the following examples without, however, limiting it thereto. All parts, ratios and percentages are by weight unless otherwise indicated. 45

#### Example 1

In a high-speed mixing apparatus (about 16,000 rev/min) at 50°C a dispersion was prepared of the following organic phase in the following aqueous phase.

50	<b>Organic Phase</b>		50
	chloroform	8 ml	
	pentaerythritol tetra-acrylate	2.05 g	
	Michler's keton	0.04 g	
	1-phenyl-1,2-propanedion-2-O-benzoyloxime (photoradical initiator)	0.304g	
55	<b>Aqueous Phase</b>		55
	5% aqueous gelatin solution	50 g	
	10% aqueous solution of lauryl-benzenesulphonic acid sodium salt	0.7 ml	

After 5 minutes of mixing the chloroform was evaporated and by addition of water the total weight of the dispersion was raised to 50 g.

- 60 The above prepared dispersion was applied to an aluminium plate at a wet coating thickness of 60

50 g per sq. m. After gelling and drying at 40—50°C the obtained photoresist layer was exposed through a transparent line original and a neutral density filter (density 1) for 5 s. In the exposure 8 Phillips (Trade Mark) TL 20 W Black Light lamps were used which lamps were placed at a distance of 10 cm from the photosensitive material.

5 After the exposure the non-exposed parts were washed-off by rubbing with foamed rubber immersed in water. 5

Thereupon the aluminium plate containing the resist pattern was put in an acid latex for 2 min, said latex being a 0.5% aqueous dispersion of copoly(acrylonitrile/butadiene/styrene) (5%/47.5%/47.5%) containing hydrochloric acid up to a pH of 1.8. The chemiphoretically treated plate 10 was rinsed with plain water and dried. The formed latex deposit was oleophilic and accepted planographic fatty ink. The residual portions of the photoresist layer were washed away with a 2% aqueous sodium hypochlorite solution (javelle water). 10

Bare hydrophilic aluminium image portions were obtained that were made more permanently repelling fatty ink by a treatment with an aqueous 2% phosphoric acid solution. The thus treated plate 15 was used for printing on a commercial offset planographic printing machine and thousands of sharp prints on offset printing paper were obtained. 15

#### Example 2

Onto a grained aluminium sheet a printed text image was deposited in the form of a silver image through the diffusion transfer reversal process (DTR-process) using a commercially available direct-positive silver halide emulsion material known as Copyproof CPRV (Copyproof is a trade mark of Agfa-Gevaert N.V., Antwerp-Belgium). 20

The exposure of said material proceeded through a transparent positive printed text original in a graphic art dark room camera.

The silver image was made hydrophobic by rubbing with a piece of cotton cloth soaked with a 25 "fixer" solution having the following composition: 25

dimethyl dodecyl ammonium chloride	2.5 g
20% aqueous solution of the sodium salt of polystyrene sulphonie acid	100 ml
potassium nitrate	12.5 g
citric acid	20 g
5% ethanolic solution of 1-phenyl-2-tetrazoline-5-thione	40 ml
sodium hydroxide	5.5 g
demineralized water	1000 ml

The sheet was immersed for 5 s into an aqueous polymer particle dispersion (latex) containing 35 30% of copoly(butadiene/methylmethacrylate/itaconic acid) (47.5/47.5/5) and having a pH of 2. 35

The thus treated sheet was rinsed with tap water and dried with a stream of hot air.

The silver image parts which were not covered by the latex were removed by etching for 30 s using an etchant having the following composition:

40 sulphanilic acid	90 g
concentrated sulphuric acid	75 ml
potassium dichromate	50 g
water up to	3 l

The sheet was rinsed and dried and formed a planographic printing form the parts of which covered with the latex polymer were accepting an oleophilic planographic ink whereas the bared aluminium parts were hydrophilic and wetted by the aqueous fountain solution of a planographic printing press. A printing run of several thousands of prints was effected with that planographic printing form. 45

#### Claims

1. A process for recording information wherein an image-wise pattern is formed on a recording material and particles are coagulated onto said image-wise pattern to form a permanent record thereof, characterized in that the said image-wise pattern is defined by metallic cations which act as a coagulant for a hydrosol, and a hydrosol which is coagulated by said ions is contacted with the said ions under conditions whereby the hydrosol becomes coagulated to define the said image-wise pattern. 50

2. A process according to claim 1, wherein the said image-wise pattern is formed by image-wise applying a liquid containing the said ions in dissolved form to the recording material. 55

3. A process according to claim 1, wherein the said image-wise pattern is formed by image-wise applying to the recording material a metal, metal oxide, metal base or metal salt, which is capable of providing said ions when in contact with the aqueous phase of the applied hydrosol.

4. A process according to claim 1, wherein said ions are derived from a source of ion-providing substance which is overall available in at least one layer or support member of said recording material and said recording material by image-wise applied activating energy is modified structurally such that an initially blocked ion-source is unblocked to deliver image-wise said ions by contact with a solvent for said ions, or modified structurally such that said source of ions is blocked image-wise so that a solvent for said ions can not reach the ion providing substance in the area of the recording material which have been modified structurally by the image-wise applied energy. 5
5. A process according to claim 4, wherein the said recording material contains a layer that initially is overall impermeable to said ions, and which becomes permeable to said ions on exposure to said activating energy. 10
6. A process according to claim 4, wherein the said recording material contains a layer that initially is overall permeable to said ions, and which becomes impermeable to said ions on exposure to said activating energy.
7. Process according to claim 1, wherein the recording material contains initially an ion-source that is capable of providing non-differentially said cations and the said material is image-wise covered with a substance blocking in the recording material the release of said ions with a solvent therefor. 15
8. A process according to any of claims 4 to 6, wherein said activating energy is activating electromagnetic radiation.
9. A process according to any of claims 4 to 6, wherein said activating energy is heat energy. 20
10. A process according to any of claims 1 to 4, wherein said recording material comprises a photo-resist layer. 20
11. A process according to claim 10, wherein said photo-resist layer covers a metallic layer which is capable of providing said ions.
12. Process according to claim 10, wherein a negative acting photoresist layer is applied onto a material which is capable of providing said ions and after image-wise photoexposure is removed in the non-exposed parts uncovering thereby portions of ion-providing material corresponding with said non-exposed parts. 25
13. Process according to claim 10, wherein a positive acting photoresist layer is applied onto a material which is capable of providing said ions and after image-wise photoexposure is removed in the exposed parts uncovering thereby portions of ion-providing material corresponding with said exposed parts. 30
14. A process according to claim 12 or 13, wherein said ion-providing material is aluminium.
15. A process according to claim 7, wherein the substance blocking the release of said cations is applied by the diffusion transfer reversal process including the producing of a silver image on an image receiving material acting here as said recording material and being capable of releasing said cations which process comprises the steps of: 35
- 1) exposing to an original a light-sensitive silver halide emulsion layer of a photographic material,
  - 2) contacting said image receiving material with the imagewise photoexposed silver halide emulsion layer while wetted with an aqueous alkaline liquid in the presence of at least one developing agent capable of reducing photoexposed silver halide to cause development of the developable silver halide and to cause undeveloped silver halide to become complexed with a silver halide complexing agent and to transfer to the image-receiving material on or in which the complexed silver halide becomes converted to a silver or silver-containing image, and
  - 3) separating said photographic and image-receiving materials. 40
16. A process according to claim 15, wherein the silver image is made hydrophobic by oxidation and by treatment with an organic compound reacting with silver ions. 45
17. A process according to claim 16, wherein said organic compounds contain a —SH, —SeH, isothiocyanate, —OH or —NH— group(s).
18. A process according to any of the preceding claims, wherein the metallic cations are multivalent metal cations. 50
19. A process according to any of claims 15 to 17, wherein the receiving material is an aluminium sheet which after removal of the silver image or hydrophobized silver image is used as planographic printing plate.
20. Recorded information obtained by a process according to any of claims 1 to 19.